A STUDY OF SOME POSSIBLE NEW METHODS FOR THE SYNTHESIS OF ETHYLENE UREA

A THESIS

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by

Henry H. Herring, Jr.

Georgia School of Technology,

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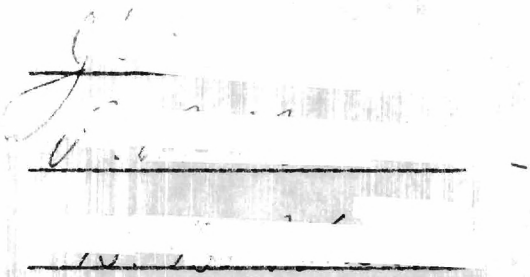
APPROVED:



ACKNOWLEDGMENT

The author wishes to express his sincere appreciation and thanks to Dr. B. B. Wroth of the Department of Chemistry and Chemical Engineering, Georgia School of Technology, for his willing guidance, helpful advice, and tactful criticism during the study of this problem. Acknowledgment is also made to the Research Division of Picatinny Arsenal, Dover, N. J., both for the suggestion of this problem and for their proposed reactions. The author also wishes to thank Dr. H. M. Waddle for the construction of certain pieces of glass apparatus.

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INTRODUCTION AND PURPOSE.

The earliest recorded synthesis of ethylene urea is that of Emil Fischer and H. Koch in 1886 (1). The work of these investigators upon this compound was very limited, and a search of the literature up to the present time reveals little knowledge of any additional investigations having been attempted for its synthesis.

The method of Fischer and Koch has been found to give good yields of ethylene urea, but the high cost of starting materials makes the production of this compound impractical on a large scale basis. Since ethylene urea is of interest today, primarily for its use as an intermediate compound in the production of the high explosive ethylene dinitroamine, this initial high cost is prohibitive.

Therefore, the chief purpose of this work is to study some possible new methods for the synthesis of ethylene urea which would entail only the use of inexpensive reagents. It is also the purpose of this work to summarize the existing literature for the methods of synthesis already known.

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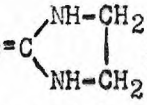
(1) Fischer and Koch, Liebig's Annalen, 232, 227 (1886).

ETHYLENE UREA.

Historical:

Ethylene urea,  , a heterocyclic compound, was first synthesized by Emil Fischer and H. Koch in 1887 (1), and their method is the one now generally used. The literature reveals no other method which compares in simplicity with theirs, though other reactions have been carried out which produce ethylene urea in various yields, a summary of which will be included in this work.

The reaction as described by Fischer and Koch, consists of refluxing an equimolecular mixture of ethylene diamine and diethyl carbonate at 180° for at least six hours, at the end of which time, the product on cooling crystallizes in white needles. The conditions for obtaining yields up to 90% from this reaction have been determined by the Research Division of Picatinny Arsenal (2), and were it not for the high cost of starting materials this method would be quite acceptable for its large scale production.

The nomenclature of ethylene urea is quite varied and it can be found in the literature under the following names: 2-keto-tetrahydroimidazol (3); 2-keto-tetrahydroglyoxaline, tetrahydroiminazolone-2 (4); N'N'Ethylene Urea, 2-oxo-imidazolidine, Imidazolidone-2 (5); ethylene carbamide (6); dihydro-2(3)-imidazolone (7).

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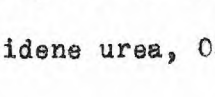
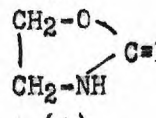
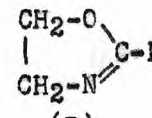
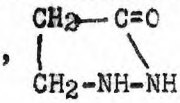
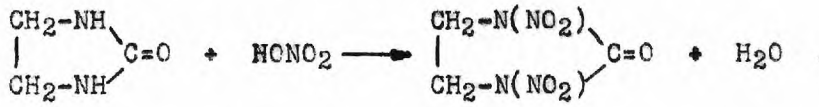
(2) Picatinny Arsenal, Dover, N. J., Communication to the Ordnance Department, Ga. School of Technology, Feb. 1938.
(3) Dictionary of Organic Compounds, Heilbron, Bunburg and Jones, Vol. II, 32.
(4) Richter's Lexicon, Vol. I, p. 105.
(5) Beilstein, 24, 2, system number 3557.
(6) Fischer and Koch, Annalen, 232, 222-228 (1886).
(7) Handbook of Physics and Chemistry, 22nd Edition, p. 768.

There are at least three isomeric compounds which appear in the literature, all of which have been well characterized. The first of these is ethylidene urea,  , melting point 154° (8). The second is ethylene pseudo urea,  or  (9), melting point

(A) (B)

190-8°. This compound is also known as ethylene isourea or the imid of the Mu oxazolidons in the case of A and the Mu amino oxazolin in the case of B (10). The third is 3(or 5)-oxo-pyrazolidine,  , a liquid with boiling point of 133-35° (11).

Ethylene urea has been well characterized and a survey of the existing literature shows it to possess the following properties: Molecular weight 86.05, m.p. 131°, crystallizes in white needles from water or chloroform, is soluble in water, hot alcohol and chloroform, and is insoluble in ether, carbon tetrachloride, carbon disulfide, and petroleum ether. It forms a dinitro derivative with fuming nitric acid, without the evolution of a gas, according to the equation:



The product crystallizes in prisms from alcohol and melts with decomposition at 210° (12). On boiling with water it decomposes into CO_2 and dinitro-ethylene diamine. It can be found described in the literature as ethylene dinitrourea, N-N'-di-nitro ethylene urea or 1-3-dinitro-imidazolidone-(2),(12).

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(8) Annalen der Chemie, 151, 204.
(9) Gabriel, Berichte, 22, 1150 (1889).
(10) Lehbruch der Organischen Chemie, Tweiter Band, Dreiter Teil, p. 523.
(11) v Rothenburg, Journal fur Praktische Chemie,2 51, 72.
(12) Franchimont and Klobbie, Recueil des travaux chimiques des Pay-Bas, 7, 6 and 243.

Recently a method for preparing this derivative has been patented by H. A. Aaronson (13), in which he avoids the use of the fuming nitric acid by using a mixed acid of 68% H_2SO_4, 22.5% HNO_3 and 9.5% H_2O. This investigator claims a 92% to 95% yield for his method, if the time for nitration is continued at least two hours, and the temperature is kept below 10°. At higher temperatures (up to 30°) the time required for the formation of the product is less, but the yields are not as favorable as those produced at the lower temperatures.

The melting point as found by Aaronson and Rinkenbach (14) is 206°, which is in fair agreement with that of Franchimont and Klobbie (210°). Aaronson and Rinkenbach have also found the compound to possess valuable explosive properties and have patented its use as an explosive mixture. When heated it undergoes explosion in five seconds at 235° to 240°. When heated at 120° it was found to be very stable, as it liberated but little gas in the course of heating for forty hours. It is soluble in acetone, but almost insoluble in ether, alcohol, benzene, carbon tetrachloride, and ethylene dichloride, and very slightly soluble in water (13).

In addition to this dinitro derivative, ethylene urea forms a picrate (15), a micro-crystalline powder, soluble in hot water and hot alcohol, with a melting point of 207-209°.

P. A. Trübsbach (16) has published a paper on the conductivity of some five membered ring compounds and he has found that aqueous solutions of ethylene urea will conduct an electric current.

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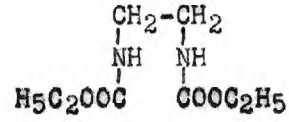
(13) Henry A. Aaronson, U. S. Patent #2,149,260, March 7, 1939.
(14) W. H. Rinkenbach and H. A. Aaronson, U. S. Patent #2,167,679.
(15) Beilstein, 24, 2, System Number 3557.
(16) P. A. Trübsbach, Zeitschrift für Physikalische Chimie, 16, 710.

An interesting and somewhat peculiar phenomenon is the formation of ethylene diurethane,



when the reaction mixture of ethylene diamine and diethyl carbonate, after refluxing for six hours, is distilled at 30 mm. pressure. This reaction or change was first observed by Fischer and Koch (17) and has since been confirmed by Franchimont and Klobbie (18). The conditions for this reaction are essentially the same as given by all these authors, but during the present study it has been found that the diurethane may even be formed without distillation at reduced pressure. For example, the diurethane and not ethylene urea was the main product formed in every case, when ethylene diamine and diethyl carbonate were refluxed under variable conditions. These conditions were such that the time of reflux varied from eight to forty hours and the temperature varied from 140° to 165°, though held constant during any one refluxing period.

This fact was disclosed through experiments designed to check the method of Fischer and Koch (1) for the synthesis of ethylene urea. Equimolecular portions of ethylene diamine and diethyl carbonate were refluxed for various periods as shown above and in each case the product was always ethylene diurethane and not ethylene urea. This fact constitutes a modification to the existing methods of preparation (18) for this compound, and particularly to that of Fischer and Koch (17) in which they specify distillation at 30 mm. pressure. Moreover, it has been found that the reaction of Fischer and Koch (1) for the synthesis of ethylene urea is limited to

(17) Fischer and Koch, Annalen der Chemie, 232, 228.
(18) Franchimont and Klobbie, Recueil des travaux des Pays-Bas, 7, 260.

six hours of reflux, when an equimolecular mixture of ethylene diamine and diethyl carbonate is used. Additional reflux time produces ethylene diurethane even when the solution is refluxed at 180°, the temperature as given by Fischer and Koch for the formation of ethylene urea. From this evidence the conclusion is reached that both ethylene urea and ethylene diurethane may be produced by refluxing a mixture of ethylene diamine and diethyl carbonate, and that the conditions for the formation of ethylene urea are much more restricted than those for the formation of ethylene diurethane. This is not to be interpreted as evidence that ethylene urea is not produced by this method but that the conditions for its synthesis are far more limited than those now given in the literature (1).

Experimental:

At the end of the reflux period described above, the reaction mixture was allowed to cool and a mass of white, needle like crystals separated out leaving a yellow colored liquor above them. The crystals were separated at the pump, washed with several portions of ether, which effectively removed all traces of the yellow color. The product was then dissolved in water and boiled with animal charcoal for a few minutes, filtered, and allowed to crystallize slowly from the water solution. This product was recrystallized from water, and long, almost colorless needles were obtained and after drying in vacuum gave a melting point of 110-110.5°, or after correction, 111.3°.

As a means of checking the constancy of this melting point, the products obtained by twice repeating the experiment described above, after separation at the pump, were recrystallized to constant melting point from alcohol and chloroform respectively, and dried in vacuum. In both instances, the melting points, coincided with that previously found when the

product was recrystallized from water. It was even found that by merely washing the crystals, as first obtained in the reaction, with small portions of ether until all traces of yellow had been removed that a pure product could be obtained. After drying in vacuum or over calcium chloride this product was found to melt at 112°.

In order to further identify the compound, several analyses for carbon hydrogen and nitrogen were determined. The results are shown in the following tables:

ANALYSIS FOR CARBON AND HYDROGEN

	WEIGHT OF SAMPLE	WEIGHT OF CO_2	WEIGHT OF WATER	% C		% H_2	
				Calc.	Found	Calc.	Found
1.	.0222	.0373	.0160	46.9	45.81	7.8	7.48
2.	.0258	.0451	.0179	46.9	47.67	7.8	7.71
3.	.0210	.0359	.0135	46.9	46.57	7.8	7.43
4.	.0343	.0577	.0232	46.9	47.31	7.8	7.48

ANALYSIS FOR NITROGEN

	WEIGHT OF SAMPLE	% N_2	
		Calc.	Found
1.	.7031	13.71	13.32
2.	.5251	13.71	12.94
3.	.5874	13.71	13.07

The analysis for carbon and hydrogen was determined by means of the simplified procedure with the semi-micro combustion apparatus described by Fieser (19) in which an ordinary analytical balance is used for weighing.

The results obtained, though not in good agreement with that calculated for ethylene diurethane, nevertheless indicate the compound to be the product sought. It is not thought that the discrepancy in the observed

(19) Fieser, L. F. "Experiments in Organic Chemistry," D. C. Heath and Co., New York 1935, p. 350.

and calculated values is due to the presence of any impurity in the compound, as each sample had been very carefully purified by repeated crystallizations from three different solvents. Therefore, the failure to obtain a more satisfactory check is believed due to an inadequacy of this method, as evidenced by the statements of Yourtee (20) and Holder (21). Both of these men, using the same method and apparatus, were unsuccessful in obtaining satisfactory checks on either known or unknown compounds.

It was found in this work, however, that by increasing the amount of oxygen many times over that as directed by Fieser, as well as by increasing the time from forty-five minutes to one and a quarter to one and a half hours, for the entire procedure, that results which more nearly check each other could be obtained on known compounds. Ten samples of known substances were first run under these conditions in order to more or less calibrate the apparatus, before any attempts to run unknown compounds were made. Special care was taken always, to follow the same procedure as nearly as possible in running each sample. Variations in the conditions on individual runs were found to give erratic results.

The analysis for nitrogen was determined by the regular Kjeldahl method, except samples not exceeding .8000 g. were used. Periods of violent bumping, with a loss of sample in some cases, were observed during the digestion of the samples with sulfuric acid, which in most cases required from six to eight hours. It is suggested that some other method be used in the future for the determination of nitrogen in ethylene diurethane, in order to avoid these inconveniences.

From the foregoing data, on percentage composition of the compound which corresponds to an empirical formula of $C_8H_{16}O_4N_2$, the melting point

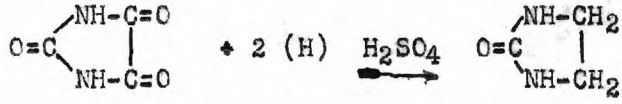
(20) L. K. Yourtee, Unpublished Thesis, - Ga. School of Technology, 1939.
(21) C. B. Holder, Unpublished Thesis, - Ga. School of Technology, 1938.

of 111.3°, its solubility in hot water and hot alcohol, and the fact that it does not form a dinitro derivative as described for ethylene urea (13) leads to the conclusion that the compound is ethylene diurethane.

PRESENT METHODS FOR THE SYNTHESIS OF ETHYLENE UREA.

In addition to the reaction already described (1) for the synthesis of ethylene urea, there are several other methods by which it can be made. Of these methods, however, there is not one by which ethylene urea can be produced sufficiently cheap to warrant its use on a commercial scale. Consequently there is a need for an economical synthesis for this compound.

The most difficult of these methods is perhaps the one which involves the electrolytic reduction of parabanic acid (22) in a sulfuric acid solution, according to the following equation:



It can also be produced by converting ethylene thiourea (23), (24) to ethylene urea by means of digesting it on the water bath with freshly precipitated HgO. The thio-compound is quantitatively converted into the oxygen compound. Another method is that of P. Pierron (25) in which he found that crystals of ethylenequanidine hydrogen bromide hold water so tenaciously that in attempting purification by distillation under reduced pressure, quantitative transformation into ammonia and ethylene urea takes place, the later product crystallizing out.

S. J. Kanewskaja (26) in an investigation on the Hoffmann reaction found that when the amide of benzoyl beta-alanine was allowed to react with

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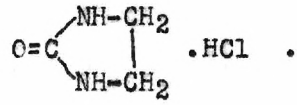
(22) Tafel and Reindel, Berichte, 34, 3288.
(23) A. W. Hoffmann, Berichte, 5, 240-2 (1872).
(24) Klut, Archiv der Pharmazie, 240, 675-77 (1902).
(25) P. Pierron, Annales de chimie, (9) 11, 361-68 (1919).
(26) S. J. Kanewskaja, Berichte, 69, 266-73 (1936).

an alkaline potassium hypobromite solution, the beta-benzoyl group was split off quantitatively and a yield of 76% tetrahydro-imidazolone or ethylene urea was obtained.

In 1937, Puschin and Mitic (27) carried out a reaction between a solution of phosgene in chloroform and ethylene diamine producing a crystalline product. This was treated with silver nitrate, forming a salt which on treatment with nitric acid was converted into silver chloride and the hydrochloride of ethylene urea,



(27) N. A. Puschin and R. V. Mitic, Annalen der Chemie, 532, 300-01 (1937)

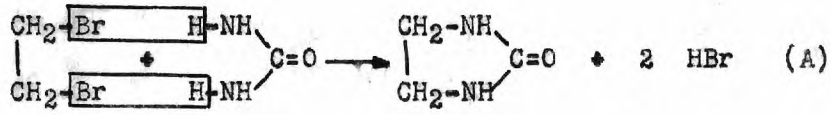
SOME POSSIBLE NEW REACTIONS FOR THE SYNTHESIS OF ETHYLENE UREA.

From the foregoing information, the need for a relatively simple and economical method of preparation for ethylene urea is obvious. Since urea is now available at a very low cost as well as certain ethylenic compounds, it was suggested by the research division of Picatinny Arsenal (2) that it might be possible to produce ethylene urea by means of a reaction or series of reactions between urea and some one of these ethylenic compounds. Consequently, attempts at a synthesis based on these suggestions as well as on some original ideas, have been carried out. These reactions as suggested by Picatinny Arsenal include: urea with each of the following ethylenic compounds: ethylene dibromide, ethylene dichloride, ethylene glycol, ethylene oxide, ethylene glycol diacetate, ethylene chlorohydrin, and ethylene glycol mono-ethyl ether. The remaining reactions were modifications of several of those listed above, in that various substances were added which might catalyse the reaction. Also included in this study are some reactions under pressure between diethyl carbonate, ammonium hydroxide, and certain ethylenic compounds. The exact procedures and conditions which were followed and maintained will be described in detail in that section allotted to each reaction.

ETHYLENE DIBROMIDE AND UREA.

Theoretical:

In this reaction an attempt was made to find suitable conditions for the removal of two molecules of hydrogen bromide with the consequent formation of the desired cyclic compound, ethylene urea. The hypothetical equation is:



Experimental:

7 g. of urea and 40 ml. of ethylene dibromide were mixed together and warmed gently in order to completely dissolve the urea. The mixture was then heated under reflux at 140° for ten hours. At the end of twenty-five minutes, the mixture began to separate into two layers, with the upper layer being colored red. At the end of two and one half hours refluxing, this red layer was approximately one-tenth of the total volume. No apparent change was visible in the lower layer at this point. After four hours the upper layer changes from a red liquid to a pale yellowish oil, containing very fine white crystals. Heating was discontinued at the end of ten hours for no further apparent change was taking place, nor was there any increase in the amount of crystalline product being formed. Ammonia was liberated during a portion of the reflux period.

This upper layer on standing over night became very hard and sticky, but when again heated to 120°, became sufficiently soft to remove from the remainder of the solution (B) by filtration. The residue was very oily and sticky, pale yellow in color, and impregnated with very small white crystals. It was treated with hot alcohol which dissolves the yellow oily

material, leaving the white crystalline product unchanged. After filtration, these crystals were washed with several small portions of alcohol (which dissolves a portion of them), recrystallized from water, and dried over calcium chloride. The resulting product failed to melt up to a temperature of 300°.

The product was found to be extremely soluble in water, sodium hydroxide, sodium bicarbonate, hydrochloric acid, and sulfuric acid. It was insoluble in chloroform, carbon tetrachloride, benzene, and only slightly soluble in ether and alcohol. With sodium hydroxide, the compound liberates ammonia, and with sulfuric acid, white vapors are formed. An aqueous solution gives with silver nitrate a yellow precipitate which is assumed to be silver bromide. An aqueous solution is also neutral to litmus. Based on this evidence and also its high melting point, the compound was characterized as ammonium bromide.

The alcoholic filtrate was allowed to evaporate, and a yellow, resinous material remained which was insoluble in water. No attempt was made to characterize this compound.

The remaining solution (B) was found to be unchanged ethylene dibromide, as evidenced by its boiling point and odor, after it had been redistilled.

From the evidence given above, the reaction did not proceed according to the equation as originally assumed. The product obtained, however, indicates that perhaps some hydrogen bromide was split out as shown in the equation (A). This would immediately react with the ammonia, which was one of the observed decomposition products of the urea, to form the ammonium bromide. The red color which first appeared in the reaction mix-

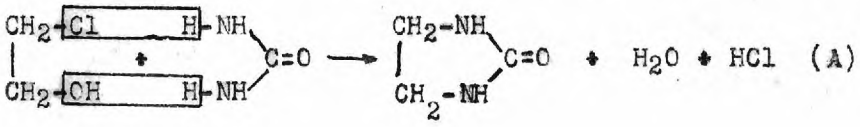
ture, seems to indicate the liberation of some bromine. The subsequent loss of this color would seem to indicate the addition of the bromine to a double bond or that the bromine acts as an oxidizing agent. This later hypothesis is more probable since carbon monoxide from the urea would easily reduce the bromine. Such a reaction would account for the formation of the bromide ions and the subsequent formation of the ammonium bromide.

The experiment was repeated under the same conditions except that ethylene dichloride was used in place of the ethylene dibromide. Similar results were obtained and the solid product formed was found to be ammonium chloride.

ETHYLENE CHLOROHYDRIN AND UREA.

Theoretical:

In this experiment an attempt was made to condense urea with ethylene chlorohydrin according to the following equation:



(A)

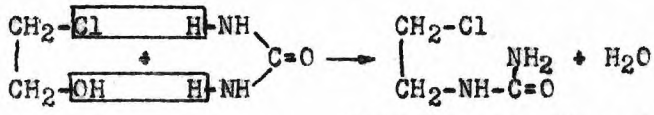
Experimental:

7 g. of urea were dissolved in 40 ml. of ethylene chlorohydrin and the mixture refluxed at 135° for eight hours. After twenty minutes of heating, the solution began to turn light yellow, and after two hours the color had changed to a light brown and the mixture was bumping somewhat violently. A white crystalline product had also begun to come down at this point. The solution gradually became darker with continued heating and at the completion of the reflux period was a deep reddish brown. The crystalline product did not change color and after cooling was separated by filtration. *After washing with several small portions of ether to remove organic material, it was recrystallized twice from water, and dried in vacuum.* It did not melt up to a temperature of 295°, but was found to sublime at temperatures above 310°. The compound was found to be very soluble in water, sodium hydroxide, sodium bicarbonate, hydrochloric acid, and sulfuric acid. It was insoluble in ether, carbon tetrachloride, chloroform, and benzene and only very slightly soluble in alcohol. An aqueous solution with sodium hydroxide liberated ammonia, and with silver nitrate formed a white precipitate, soluble in ammonium hydroxide, and reprecipitated upon the addition of nitric acid. Concentrated sulfuric acid on a portion of the solid, liberated a gas

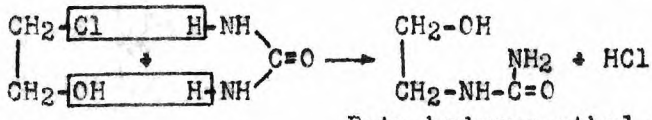
which turned moist litmus paper red. Based on this evidence, the compound was characterized as ammonium chloride.

The original filtrate was distilled at 75 mm. pressure, and the main fraction boiled between 68° and 70°. When this boiling point was corrected to standard pressure by means of the formula of Hass and Newton (28) it was found to be 130°, which is in close agreement with that for ethylene chlorohydrin (128°). The boiling range for the next fraction was 70° to 75°. It was water white and completely miscible with water. It was not characterized further. The residue in the flask (3 ml.) is a thick, oily red liquid which was not analyzed.

Here again the reaction did not proceed as it had been indicated in the equation (A). The formation of ammonium chloride would seem to indicate that this reaction was very similar to those of the two preceding experiments, and consequently all three must proceed through somewhat the same mechanism as previously outlined in the experiment with ethylene dibromide. It is conceivable that either a molecule of hydrogen chloride or water alone was lost which would give rise to the following compounds:



Beta-chloro-ethyl urea

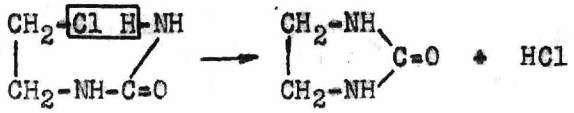


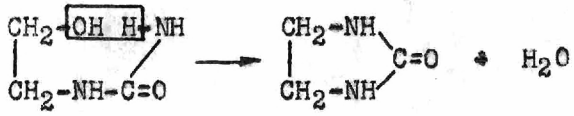
Beta-hydroxy-ethyl urea

If this were true, then it is even more conceivable that each of these compounds should in turn lose an additional molecule of hydrogen

(28) H. B. Hass and R. F. Newton, Handbook of Chemistry and Physics, 22nd Edition, p. 1298.

chloride or water, through distillation at reduced pressure or by the addition of a suitable dehydrating agent, to complete the ring closure and produce the desired ethylene urea. The representative equations for these changes are as follows:

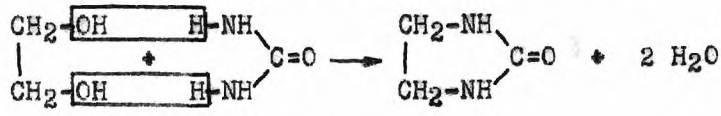




ETHYLENE GLYCOL AND UREA.

Theoretical:

In this reaction, as in the preceding ones, ring closure was attempted by the elimination of two molecules of water between ethylene glycol and urea as indicated in the following equation:



The reaction was tried both with and without the use of a dehydrating agent. The elimination of a molecule of water or even two molecules by the use of phosphoric anhydride has been used successfully to form cyclic compounds in similar cases.

Experimental:

7 g. of urea were dissolved in 50 ml. of ethylene glycol and gently refluxed for approximately twenty hours. The reaction mixture assumed, almost immediately, a pale yellow color which did not change on continued boiling and on standing. Ammonia was liberated and could be detected at the top of the condenser during the first three hours of refluxing. No solid material appeared in the flask during the entire reflux period, however, the condenser soon became coated with a white solid which is assumed to be urea which has sublimed at the temperature (210°) of the reaction.

After twenty hours of boiling, the solution was cooled and allowed to stand over night. No solid material separated out, therefore in order to concentrate the solution, it was distilled at 75 mm. pressure. No distillate came over until 100° had been reached. From 100° to 140°, however, a 25 ml. water white fraction was removed. The boiling point of this frac-

tion was never constant but continued to rise slowly to 140° at which temperature no more distillate was obtained. This fraction was thought to be, for the main part, ethylene glycol on the basis of solubility tests and its reaction with acetyl chloride.

The solution was then heated up to 160° and no more distillate was obtained. However, violent bumping set in, even though an ebulution tube was used in the flask. Distillation was discontinued, and after cooling, no solid appeared in the solution. The high boiling residue was a deep reddish brown liquid, miscible with water and alcohol. It has not been characterized further. This experiment was repeated with the addition of 3 g. of phosphoric anhydride to the reaction solution. After several hours refluxing, the only apparent change was the light yellow or amber color which the solution had assumed. After cooling and standing for several days, no crystals appeared. The solution was then distilled under reduced pressure; two water white fractions were obtained, both having a very noticeable odor of ammonia. They were miscible with water and alcohol, and an aqueous solution was basic to litmus and liberated ammonia when treated with sodium hydroxide. There was no precipitate with silver nitrate when the solution was made acid with nitric acid. With barium chloride a white floculent precipitate was formed which was soluble in nitric acid. The products were not characterized further.

The high boiling fraction (above 160° at 75 mm.) was an odorless, very viscous, oily, red liquid. It was miscible with water and soluble in sulfuric acid and also sodium hydroxide but without the liberation of ammonia. It is insoluble in benzene, ether, and chloroform. An aqueous solution is acid to litmus.

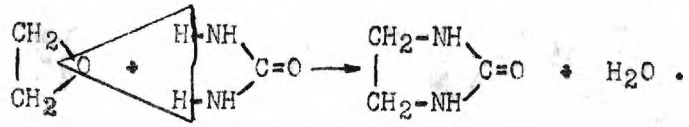
Discussion:

Here again the reaction did not proceed as indicated. The liberation of ammonia during the refluxing, and also during the distillation, seemed to indicate either decomposition of the urea, or decomposition of some product into which it may have been rearranged at the temperature of the experiment. The fact that no urea could be recovered also indicates either complete decomposition or the formation of some other product. The large amount of ammonia given off seems to favor the former assumption.

ETHYLENE OXIDE AND UREA.

Theoretical:

The desired reaction in this experiment was as follows:



Once again the problem is one of elimination of water between ethylene oxide and urea, in order to have ring closure take place. The problem might also be considered in this, as well as the other experiments, as the joining of carbon to nitrogen to carbon in order to form a cyclic compound. In this experiment anhydrous zinc chloride and phosphoric anhydride were used as dehydrating agents.

Previously, ethylene oxide has been condensed with urea (29) but not in the manner as indicated in the above equation. The product obtained was not acyclic and after acylation with an acid, derived from a natural fat, it was found to be useful as a wetting agent.

Experimental:

To facilitate the handling of the ethylene oxide, a special container was made as follows: a glass delivery tube, equipped with a stop-cock, was sealed onto the neck of a 250 ml. round bottom flask. About 2.5 cm. *from the neck of the flask, an inlet tube 6" in length was sealed into the flask. This tube had a constriction midway, at which point it was sealed* off after the flask had been filled with ethylene oxide. Wide rubber bands were used to hold the stop-cock in place.

In order to reflux ethylene oxide, very low temperatures had to be maintained in the condenser in order to prevent loss of the solvent by

(29) Henry A. Piggot, British Patent 432,356, July 22, 1922.

evaporation. A special condenser was used in which dry ice and chloroform were the cooling medium. This condenser was made by sealing the mouth end of an ordinary 10" test tube (25 mm. diameter) inside a 40 mm. glass tube, which is 12" in length. The bottom of this outside tube was drawn out to a diameter of 12 mm. and then a six inch neck, of this diameter, was sealed onto the condenser. At the top of the outside jacket a small outlet tube is let in for the escape of the vapors which fail to condense. Dry ice is used in the 10" test tube and the vapors rising around it are condensed.

5 g. of urea and 1 g. of phosphoric anhydride were intimately mixed and placed in a small three necked flask, carrying the condenser described above. An attempt was made to introduce ethylene oxide into the flask, and instantly upon its contact with the mixture of urea and phosphoric anhydride, ignition spontaneously occurred. The results were the same when the amount of phosphoric anhydride was reduced as low as .2 g.

The experiment was repeated using anhydrous zinc chloride in place of the phosphoric anhydride. Very little heat was generated in this reaction, and in order to reflux the mixture, gentle heat was applied up to 40°. The mixture was never completely in solution, even upon addition of approximately 20 ml. excess of ethylene oxide.

The reaction mixture was boiled gently for an hour at the end of which time the flask contained a milky, white, amorphous material, as well as some excess ethylene oxide. The solid was separated and found to be insoluble in hot and cold water, alcohol, ether, benzene, carbon tetrachloride, and chloroform. It is soluble in sulfuric acid, nitric acid, and sodium hydroxide. When heated with sodium hydroxide, it does not liberate ammonia. An attempt was made to extract with chloroform, any ethylene urea

which might have been formed. Several extractions failed to yield any solid material whatsoever after evaporation of the solvent.

The solid which was left in the flask at the end of the reaction, seemed to be a mixture of at least two substances, and all efforts to separate the compounds by solvent extraction failed completely. Consequently, no satisfactory melting point was obtained, though the impure product itself does not melt up to 300°, and at much higher temperatures, sinters and chars, without completely melting.

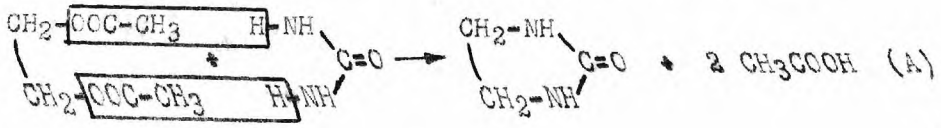
Discussion:

From these facts it was concluded that no ethylene urea was obtained by this method. It is evident that a reaction took place between the materials, and most probably between all three of the reactants. The extreme volatility and inflamability of ethylene oxide make it very difficult to carry out experiments with this reagent where it is necessary to reflux the mixture.

ETHYLENE GLYCOL DIACETATE AND UREA.

Theoretical:

This experiment was undertaken in an effort to produce ethylene urea by the reaction of a derivative of ethylene glycol and urea. When this derivative is the diacetate, this resolves into the elimination of two molecules of acetic acid as shown in the following equation:



These materials were refluxed alone, then the experiment was repeated using small amounts of both concentrated sulfuric and hydrochloric acids, in an effort to catalyse the reaction.

Experimental:

10 g. of urea were dissolved in 50 ml. of ethylene glycol diacetate and refluxed for three hours. Solution did not change color, but a few white crystals settled out after cooling. These were separated and found to be insoluble in ether, alcohol, chloroform, carbon tetrachloride, sulfuric acid, sodium bicarbonate, and sodium hydroxide. They were readily soluble in hot water but almost insoluble in cold water. An aqueous solution is neutral to litmus and when treated with sodium hydroxide no ammonia was liberated. The compound gives every indication of being inorganic in nature, particularly in regard to melting point. Up to 300° it did not melt at all, but finally sublimed at higher temperatures. An aqueous solution with silver nitrate gives a white coagulated precipitate which is greatly intensified by the addition of ammonium hydroxide, but completely soluble in nitric acid. The crystals were dissolved in water and shaken with several portions

of chloroform, in an attempt to extract any ethylene urea which might have been formed. On evaporation of the chloroform, only a minute amount of residue was left.

When sulfuric acid or hydrochloric acid were added to the reaction mixture as described above, a white solid began to form almost immediately; the addition of more acid increasing the amount of solid which separates out. In each case, after separation of the crystals, they were identified and found to be ammonium sulfate and ammonium chloride, respectively.

The filtrates left after the separations were made smelled distinctly of acetic acid, and were a light amber color. Each of them is distilled under reduced pressure and acetic acid, ethylene glycol diacetate, and a high boiling residue were obtained. This residue in both cases is a red, viscous, oily material which is probably a mixture of ethylene glycol and decomposition products of urea.

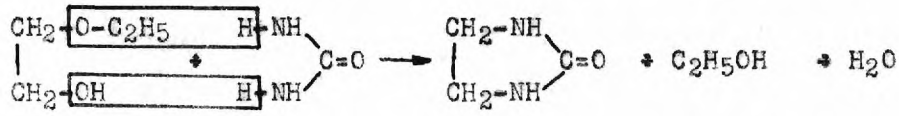
Discussion:

From the foregoing data, it would seem that the acetic acid had been formed, but from the hydrolysis of the diacetate by the acids added, rather than from the reactants as shown in the equation (A). The presence of the ammonium salts certainly indicates the decomposition of the urea. It is conceivable that after the hydrolysis of the diacetate that the resulting acetic acid might react with the urea to form acetyl or diacetyl urea. However, there is no evidence of this having occurred.

ETHYLENE GLYCOL MONO-ETHYL ETHER AND UREA.

Theoretical:

In this experiment a derivative of ethylene glycol was again used in an attempt to form ethylene urea as shown in the equation:



This would involve the elimination of both a molecule of ethyl alcohol and water in order to form the compound desired. This method has the disadvantage of forming alcohol as a by product which will in turn react with ethylene urea to form ethylene diurethane if the two are heated for more than six hours as already discussed previously in this work.

Experimental:

10 g. of urea were dissolved in 50 ml. of ethylene glycol mono-ethyl ether and then refluxed at 160° for eighteen hours. During the heating, some urea sublimed into the condenser, and the solution assumed a pale yellow color almost the same shade as that described in the previous experiments.

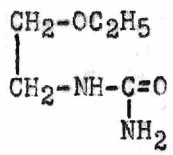
On cooling no solid appeared, and even after concentration of the solution by distillation at reduced pressure, no solid appeared.

Discussion:

There was no evidence that ethylene urea was formed under these conditions. However, there was scarcely no odor of ammonia being liberated during this reaction, which seems to indicate less decomposition than in the preceding cases.

Here again there is the possibility of the elimination of only the

molecule of water to give the following compound:



Beta- ethyoxy-ethyl urea

This compound has not been characterized but it seems probable that this reaction offers a possible method for its synthesis.

DIETHYL CARBONATE; ETHYLENE DIBROMIDE AND AMMONIUM HYDROXIDE.

Theoretical:

This experiment was carried out under pressure in a small Parr bomb. In this case an attempt was made to form ethylene urea through a series of continuous reactions in the bomb. It was hoped that the ammonia would react with the dibromide to form ethylene diamine and that this would in turn react with the diethyl carbonate to produce ethylene urea.

The factilities on hand and the time available did not permit complete investigation of the possibilities of this method. But it seems to offer a means of solving this problem, for in the experiments tried, a white crystalline product was obtained in each case. This was not ethylene urea but it is believed likely that with further investigation, the conditions favorable for the formation of the compound may be found.

Experimental:

Small amounts of diethyl carbonate, ethylene dibromide and ammonium hydroxide were heated together for a few minutes in the Parr bomb. Much difficulty was encountered in finding a suitable gasket which would withstand the corrosion of the reactants at the temperature and the pressure of the reaction. The products were all found to be greatly contaminated with iron compounds, which made purification much more involved. The experiment was repeated using ethylene dichloride and ethylene chlorohydrin in place of the dibromide.

After separation of the solids, using ether to remove organic material and iron compounds, a white crystalline product was obtained in each case. Recrystallization from water several times gives a product insoluble in the common organic solvents and soluble in sodium hydroxide,

hydrochloric acid, and sulfuric acid. An aqueous solution gives with silver nitrate a white precipitate, insoluble in nitric acid, soluble in ammonium hydroxide. With sodium hydroxide, an aqueous solution when heated liberates ammonia. The product does not melt up to 280°, but sublimes when heated on a spatula at higher temperatures.

Attempts were made to extract any ethylene urea, which might have been formed, with chloroform, but after concentration of the extracts no residue remained. This again indicates that the reaction failed to give ethylene urea, even as all the preceding ones failed to yield it.

SUMMARY.

I. The history and nomenclature of ethylene urea has been reviewed.

II. Existing methods for the preparation of ethylene urea have been summarized.

III. Ethylene urea has been prepared by the method of Fischer and Koch, and the conditions found to be limited to not more than six hours of heating and a temperature of not less than 180°. Otherwise, ethylene diurethane is the product formed even without distillation at reduced pressure as given by Fischer and Koch.

IV. Nine different attempts for the synthesis of ethylene urea have been described in detail. Each of these reactions is between some ethylenic compound and urea, combined with different catalytic agents, with the exception of the last one. This last experiment is an attempt at a synthesis under pressure using diethyl carbonate, ammonium hydroxide, and some ethylenic compound.